

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

## The Kinetics of the Decomposition of Certain Salts of Trichloroacetic Acid in Ethanol-Water Mixtures<sup>1,2</sup>

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It was proposed, in a study of the decomposition of trichloroacetates in several solvents,<sup>4</sup> that the rate determining step is the decomposition of the trichloroacetate ion, forming carbon dioxide and the anion of the acid chloroform,  $\text{CCl}_3^-$ . This hypothesis was examined for various amine salts of trichloroacetic acid<sup>5</sup> and the similar hypothesis for the decomposition of trinitrobenzoates in alcohol<sup>6</sup> and in dioxane-water mixtures<sup>7</sup> has also been investigated. The investigation of the trichloroacetate decomposition<sup>4</sup> indicated that while sodium trichloroacetate decomposed more slowly in water than in ethanol, the rate was higher in a 95% ethanol mixture of ethanol and water than in either pure solvent. However, no other solvent mixtures were investigated and the exact solvent composition corresponding to the maximum rate remained undetermined. This paper reports the results of measurements of the rate of decomposition of sodium trichloroacetate in 0.01 and 0.1 *M* concentration over the whole range of solvent composition and in 0.02 and 0.05 *M* concentrations in the high alcohol range, together with similar measurements on lithium trichloroacetate and some results on barium, calcium, tetraethylammonium and tetraethanolammonium trichloroacetates.

The salts used were prepared by neutralizing the hydroxide or carbonate of the desired cation with a water solution of purified trichloroacetic acid. This solution was evaporated to dryness at room temperature and the crude salt recrystallized from absolute alcohol in a Dry Ice-acetone-bath. The ethanol was prepared by refluxing absolute alcohol over calcium oxide and distilling from the oxide. The ethanol-water mixtures were prepared by adding a measured amount of water to a weighed amount of ethanol. This operation, as well as the preparation and dispensing of the solutions, was carried out in an all-glass apparatus designed to preclude the entrance of water vapor from the air. The measurement of the decomposition velocity was carried out by titration of the amount of bicarbonate formed in a manner similar to that previously described.<sup>4,7</sup> In solutions of high water content it was also necessary to determine the amount of chloride ion formed by the hydrolysis of the chloroform.

### Results

The rate of decomposition of sodium trichloroacetate was investigated over the whole range of

(1) From a dissertation submitted by George A. Hall, Jr., to the Graduate School of The Ohio State University, in 1945, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Presented before the Division of Physical and Inorganic Chemistry at the 109th Meeting of the American Chemical Society, Atlantic City, N. J., April 9, 1946.

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(4) Verhoek, *THIS JOURNAL*, **56**, 571 (1934).

(5) Verhoek, *ibid.*, **67**, 1062 (1945).

(6) Verhoek, *ibid.*, **61**, 186 (1939).

(7) Trivich and Verhoek, *ibid.*, **65**, 1919 (1943).

solvent composition at temperatures of 50 and 60° for initial salt concentrations of 0.01 and 0.1 *M*, as well as in solvents of 100, 97, 95 and 90% ethanol for initial concentrations of 0.02, 0.05 and 0.01 *M* with added 0.1 *M* sodium thiocyanate. These data are given in Tables I and II and those for 60° are plotted in Fig. 1. It was

TABLE I

THE EFFECT OF CHANGING SOLVENT COMPOSITION ON THE DECOMPOSITION OF SODIUM TRICHLOROACETATE

#### A. Initial Concentration 0.01 *M*

Alcohol, %	Concn. m./l. $\times 10^3$	$k_{50^\circ}$ sec. <sup>-1</sup> $\times 10^4$	$k_{60^\circ}$ sec. <sup>-1</sup> $\times 10^5$	$E_{50-60}$ cal.
100	8.90-9.36	10.73 $\pm$ 0.15 <sup>4</sup>	2.60 $\pm$ 0.04 <sup>3</sup>	30,300
97	9.20-9.80	10.28 $\pm$ .06 <sup>3</sup>	2.32 $\pm$ .12 <sup>2</sup>	31,800
95	9.80-10.05	9.62 $\pm$ .02 <sup>2</sup>	2.18 $\pm$ .01 <sup>2</sup>	31,800
90	9.99	8.62	1.887	32,500
80	10.20	6.11	1.338	32,500
60	10.13	3.30	0.670	34,100
40	9.37	1.759	.339	35,200
20	9.72-10.70	0.712 $\pm$ 0.015 <sup>2</sup>	0.1254 $\pm$ 0.0069 <sup>2</sup>	37,100
0	9.22-10.00	.338 $\pm$ .030 <sup>2</sup>	.0541 $\pm$ .0024 <sup>2</sup>	39,200

<sup>a</sup> The superscripts on the average deviations indicate the number of duplicate experiments.

#### B. Initial concentration 0.1 *M*

% Alc.	Concn.	$k \times 10^4$ sec. <sup>-1</sup> (60°)	$k \times 10^5$ sec. <sup>-1</sup> (50°)	$E_{50-60}$ (cal.)
100	0.0946	5.58	1.322	30,800
97	.0906	6.40	1.387	32,700
95	.0944	6.43	1.385	32,800
90	.0900	6.08	1.331	32,500
80	.0879	4.96	1.039	33,400
60	.0923	2.93	0.582	34,600
40	.0920	1.612	.309	35,300
20	.0932	0.640	.1267	34,600
0	.0902	0.355	.0605	37,800

TABLE II

DECOMPOSITION OF SODIUM TRICHLOROACETATE IN VARIOUS SOLUTE CONCENTRATIONS

#### A. Decomposition of 0.05 *M* $\text{CCl}_3\text{COONa}$

% Alc.	Concn.	$k \times 10^4$ sec. <sup>-1</sup> (60°)	$k \times 10^5$ sec. <sup>-1</sup> (50°)	$E_{50-60}$ (cal.)
100	0.0469	7.32	1.531	33,500
97	.0493	7.55	1.527	34,200
95	.0292	8.58	1.520	37,000
90	.0483	6.68	1.535	31,500

#### B. Concentration of 0.02 *M* $\text{CCl}_3\text{COONa}$

100	0.0181	9.46	2.14	31,800
97	.0195	8.97	1.866	33,600
95	.0193	8.68	1.888	32,600
90	.0186	8.08	1.779	32,400

#### C. Decomposition of 0.01 *M* $\text{CCl}_3\text{COONa}$ + 0.1 *M* NaSCN

100	0.1144	4.96	1.139	31,500
97	.1151	5.01	1.221	30,200
95	.1144	5.17	1.213	31,000
90	.1144	4.92	1.113	31,800

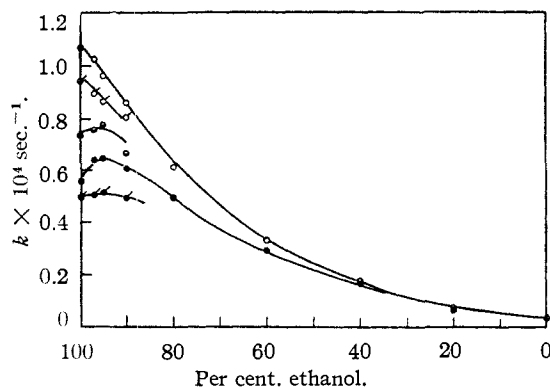


Fig. 1.—The effect of changing the solvent on the rate of decomposition of sodium trichloroacetate at 60°, initial concentration:  $\circ$  0.01  $M$ ;  $\square$  0.02  $M$ ;  $\bullet$  0.05  $M$ ;  $\blacksquare$  0.1  $M$ ;  $\blacktriangle$  0.01  $M$  + 0.1  $M$  NaSCN.

found that in solutions of 0.01 and 0.02  $M$  initial concentration the value of the specific rate constant decreased steadily as the amount of water in the solvent was increased. For initial concentrations of 0.05, 0.1 and 0.01  $M$  with added inert salt the value of the rate constant increased as the first amount of water was added, passed through a maximum at about 95% ethanol, and then decreased as for the lower concentrations. All individual experiments gave good first order rate constants; these were independent of the initial salt concentration in 100% water but decreased with increasing salt concentrations for solvents of high ethanol content. The activation energies showed a steady increase as the water content was increased, though the values in pure water reported here are probably too high. The earlier value of 36,000 calories obtained by Verhoek<sup>4</sup> for 0.1  $M$  sodium trichloroacetate over a 40° temperature range is doubtless more nearly correct.

Lithium trichloroacetate was found to behave in a manner similar to sodium trichloroacetate (Table III). In solutions of 0.1  $M$  initial concentration the rate constant increased as water was added to the ethanol, passed through a maximum at about 95% ethanol, and then decreased. In solutions of 0.01  $M$  initial concentra-

TABLE III  
THE VELOCITY OF DECOMPOSITION OF LITHIUM TRICHLOROACETATE

% Ethanol	A. Initial Concentration 0.01 $M$		$E_{50-60}$ (cal.)
	$k \times 10^5 \text{ sec.}^{-1}$ (60°)	$k \times 10^5 \text{ sec.}^{-1}$ (50°)	
100	13.01	2.61	34,300
97	11.46	2.36	33,800
95	10.28	2.31	31,900
90	9.14	1.97	32,800
B. Initial Concentration 0.1 $M$			
100	6.82	1.556	31,600
97	7.36	1.575	32,900
95	7.26	1.557	32,900
90	6.81	1.434	33,300

tion the value of  $k$  decreased as water was added. The rate was faster in the more dilute solutions. In general the rate constants were higher than the values for the sodium salt at corresponding concentrations and solvent compositions.

Some work was also carried out using calcium, barium, tetraethylammonium, and tetraethanolammonium trichloroacetates. It was found that the quaternary ammonium salts decomposed at rates higher than did the lithium and sodium trichloroacetates while the salts of the bivalent ions decomposed at a lower rate (Table IV).

TABLE IV  
THE VELOCITY OF DECOMPOSITION OF SEVERAL SALTS OF TRICHLOROACETIC ACID IN 0.01  $M$  SOLUTIONS

Salt	Ethanol, %	Temp., °C.	$k \times 10^5 \text{ sec.}^{-1}$
$(\text{CCl}_3\text{COO})_2\text{Ba}$	100	70	6.40
	100	70	5.55
	95	70	17.50
$(\text{CCl}_3\text{COO})_2\text{Ca}$	100	70	1.36
	0	70	1.36
	0	70	1.36
$\text{CCl}_3\text{COON}(\text{C}_2\text{H}_5)_4$	100	70	100
	100	50	4.46
	65	50	0.655
$\text{CCl}_3\text{COON}(\text{C}_2\text{H}_4\text{OH})_4$	100	50	0.130
	0	50	0.130
	0	50	0.133

Calcium trichloroacetate exhibited a maximum in rate constant upon passing from ethanol to water even in the 0.01  $M$  solutions (in trichloroacetate ion). Complete data were not taken for the other salts.

In 100% ethanol the rate constant decreased with the cation used in the order tetraethylammonium, tetraethanolammonium, lithium, sodium, barium and calcium. In pure water, too, the quaternary ammonium salts showed the most rapid decomposition.

Several experiments were carried out in which anilinium benzenesulfonate was added to the sodium trichloroacetate solution. It was found that the addition of 0.01  $M$  anilinium ion to a 0.01  $M$  sodium trichloroacetate solution in ethanol lowered the rate constant from  $1.073 \times 10^{-4} \text{ sec.}^{-1}$  to  $7.97 \times 10^{-5} \text{ sec.}^{-1}$ . If as has been suggested<sup>8</sup> the reaction were a pseudo-unimolecular one in which the trichloroacetate ion reacted with a proton-containing solvent, the addition of the proton donor, anilinium ion, might have been expected to speed up the reaction; actually a decrease in rate was observed. The decrease is the result of the neutralization of anilinium ion by trichloroacetate ion, forming undissociated and stable trichloroacetic acid.

### Discussion

Although each individual experiment produced a good first order rate constant, in solvents of

(8) Glasstone, Laidler and Eyring, "The Theory of Rate Processes," D. Van Nostrand Co., New York, N. Y., 1941, p. 415.

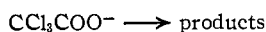
high ethanol content the value of the rate constant varied with the initial salt concentration. When the logarithm of the rate constant is plotted against the square root of the concentration, straight lines with a negative slope are obtained. While this is the expected result if the rate-determining step is a reaction between two oppositely charged ions, the slopes of these curves are much too small to allow of that interpretation, their absolute values being of the order of one-sixth those of the theoretically predicted slopes for such a reaction at the solvent compositions used.

If, however, the assumption is made that the decrease in rate with increasing concentration is due to the association of the electrolyte into ion pairs which react at a negligible rate compared to that of the free ion, then the curves mentioned may be used empirically for extrapolation back to infinite dilution to obtain the velocity constant for the decomposition of the free ion. With this value and the measured values at finite concentrations, dissociation constants for the ion pairs may be calculated.

The concentration of the free trichloroacetate ion in any solvent mixture is given by

$$x = \frac{1}{2}[-K + \sqrt{K^2 + 4Kc}] \quad (1)$$

where  $c$  is the stoichiometric concentration of the salt and  $K$  is the dissociation constant of the ion pairs into free ions. If the only reaction occurring is



its rate may be expressed as

$$\text{rate} = k_{\text{ion}} [\text{CCl}_3\text{COO}^-] = \frac{1}{2}k_{\text{ion}} [-K + \sqrt{K^2 + 4Kc}] \quad (2)$$

where  $k_{\text{ion}}$  is the rate constant of the free ion. However the rate of reaction as measured is expressed by

$$\text{rate} = kc \quad (3)$$

where  $k$  is the measured rate constant at concentration  $c$ . By equating (2) and (3) and solving for  $K$  it is found that

$$K = \frac{k^2c}{k_{\text{ion}}} (k_{\text{ion}} - k) \quad (4)$$

Dissociation constants for the ion pairs calculated from  $k$ ,  $c$  and the extrapolated value,  $k_{\text{ion}}$ , are given in Table V.

TABLE V  
DISSOCIATION CONSTANTS OF SODIUM TRICHLOROACETATE  
IN ETHANOL-WATER MIXTURES AT 60°

% Ethanol	$K_{0.01}$	$K_{0.02}$	$K_{0.05}$	$K_{0.1}$	$K_{\text{ave.}}$
100	0.020	0.023	0.025	0.024	0.023
97	.035	.034	.044	.047	.040
95	.037	.040	.057	.062	.049
90	.045	.055	.059	.078	.059

These values show an increase with increasing water concentration as should be expected and

are in good agreement with known dissociation constants of strong electrolytes in ethanol.<sup>9</sup> Hence the assumption that associated trichloroacetate ions do not decompose seems to be a good one. Substitution of equation (4) into equation (2) shows the dependence of the rate of reaction upon the first power of the concentration and thus explains the first order rate constants of individual experiments.

For the solvent mixtures containing less than 90% alcohol, in which complete data were not taken, a linear relationship between  $\log k$  and  $\sqrt{c}$  was assumed, and the values of  $k_{\text{ion}}$  at zero concentration calculated. These values are given in Table VI and Fig. 2 which shows a logarithmic

TABLE VI  
RATE CONSTANTS FOR THE DECOMPOSITION OF THE TRICHLOROACETATE ION AT 60°

% Ethanol	$K_{\text{ion}} \times 10^5 \text{ sec.}^{-1}$
100	14.34
97	12.60
95	11.80
90	10.24
80	6.80
60	3.50
40	1.83
20	0.724
0	.374

relationship between the rate constant for the free ion and the solvent composition.

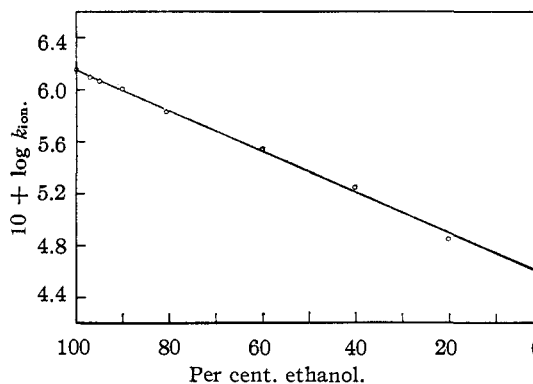


Fig. 2.—The effect of changing the solvent on the rate constant for the trichloroacetate ion at 60°.

On the basis of the postulation that ion pairs do not react it is possible to explain the variation of the rate constants for the different salts in ethanol. Barak and Hartley<sup>10</sup> report that in alcohol the lithium ion is more highly solvated, and hence of larger size, than is the sodium ion. This larger size would lead to a greater degree of dissociation of the ion pairs of lithium trichloroacetate and hence a higher rate of decomposition, as was observed. The tetraethanolammonium ion is probably quite large hence its trichloroac-

(9) Bezman and Verhoek, *THIS JOURNAL*, **67**, 1330 (1945).

(10) Barak and Hartley, *Z. physik. Chem.*, **165A**, 272 (1933).

tate is only slightly associated and should give a large value for the rate constant. However, the tetraethylammonium ion is reported to be quite small in ethanol and hence its salts should be highly associated, yet its trichloroacetate decomposed more rapidly than any of the other salts of univalent ions. No satisfactory explanation for this anomalous result can be given.

The salts of bivalent ions should be expected to be more associated than those of univalent ions and hence the barium and calcium trichloroacetates should decompose at lower rates than does sodium trichloroacetate, as observed.

The increase in activation energy as the amount of water in the solvent increases has been attributed to the difference in the solvation of the trichloroacetate ion in the two media.<sup>4</sup> The trichloroacetate ion is presumed to be more readily hydrated than alcoholated, and since this hydration is probably an exothermic process the activation energy is increased by the heat of hydration.

By a consideration of the changes occurring when water is added to the alcohol it is possible to explain the occurrence of a maximum in the rate constant. First, the addition of the water will increase the activation energy and hence decrease the rate constant. Second, the addition of the first traces of water will hydrate the cation in preference to the anion since it is the smaller of the two ions. Hydration of the cation will increase the microscopic dielectric constant in the immediate vicinity of the ion pairs and produce greater dissociation. This will cause the rate constant to increase. The net effect of adding water to the ethanol, then, will depend upon the relative magnitudes of these two opposing effects.

In solutions of 0.1 *M* initial concentration as the first trace of water is added, there are insufficient water molecules present to hydrate the trichloroacetate ion to an extent great enough to overcome the increase in rate constant due to decreased ion association. Hence the rate constant will increase. As more water is added more and more trichloroacetate ions become hydrated and the effect of increasing the activation energy becomes more important. This causes the rate constant to pass through a maximum and then decrease to a lower value in water than in ethanol.

In solutions of 0.01 *M* initial concentration, as well as in the infinitely dilute solutions, the first

water added will be sufficient to cause the decrease in rate constant due to increased hydration of the trichloroacetate ion to predominate. Hence the rate constant will show only a decrease. In a 97% ethanol solution of 0.01 *M* sodium trichloroacetate the ratio of water molecules to the stoichiometric trichloroacetate concentration is the same as it is in an 80% ethanol solution of 0.1 *M* concentration where the effect causing the maximum has already been overcome.

### Summary

1. The rate constants for the decomposition of tetraethylammonium, tetraethanolammonium, lithium, sodium, barium, and calcium trichloroacetates were measured in 100% ethanol and found to decrease for the different salts in the above order.

2. At initial concentrations of 0.01 *M* the rate constant for sodium trichloroacetate decreased regularly upon increasing the amount of water in the solvent. At initial concentrations of 0.1 *M* it was found that the rate constants increased to a maximum at 95% ethanol as water was added and then decreased. In 100% ethanol the rate constant decreased with increasing initial salt concentration while in water it was independent of it.

3. The activation energies of the reaction were found to increase as the water content was increased.

4. The concentration effect has been related to the differences in ion association into ion pairs at the different concentrations. Values for the limiting rate constants in infinitely dilute solutions and for the dissociation constants of the ion pairs have been calculated.

5. The variation of the rate constant for the different salts has been related to the number of ion pairs formed in each case.

6. The variation of activation energy has been related to the varying degrees of solvation of the trichloroacetate ion.

7. The appearance of the maximum in the rate constants has been attributed to a competition between the decrease in ion association due to an increase in dielectric constant and the increase in hydration of the trichloroacetate ion as the amount of water is increased.